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The three objectives of this work are to determine the nature of highly vibrationally excited polyatomic molecules, to determine the rate constants and pathways for the collisional relaxation of these molecules, and to probe the electronic spectroscopy of these molecules. We have created and implemented approaches for accomplishing these objectives and have demonstrated their feasibility by studying the collisional energy transfer in highly vibrational excited acetylene. We have found that the collisional self-relaxation rates of single angular momentum states with 10 000 cm^{-1} of vibrational energy are a substantial fraction of the gas kinetic collision rates. The rate constant is about a factor of two smaller for relaxation by atomic partners.

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between 300 and 700 K. J. M. Robinson, D. J. Pearson,
R. A. Copeland, and F. F. Crim, J. Chem. Phys. 82, 780 (1985).

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Collisional Relaxation of Single Rotational States in Highly
Vibrationally Excited Acetylene. E. Carrasquillo M., A.L. Utz,
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ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The three objectives of this work are to determine the nature
of highly vibrationally excited polyatomic molecules, to
determine the rate constants and pathways for the collisional
relaxation of these molecules, and to probe the electronic
spectrosocpy of these molecules. We have created and
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INTRODUCTION

Collisional energy transfer is the means by which molecules acquire and lose the large amounts of vibrational energy involved in many chemical reactions, particularly those requiring or releasing substantial energy. Understanding the details of collisional energy redistribution among the internal degrees-of-freedom of highly excited molecules and transfer to those of their collision partners is essential to unraveling the complex physical and chemical processes involved in combustion, atmospheric chemistry, the operation of molecular lasers, and many other systems in which highly energized molecules participate. Collisional energy transfer provides the energized species for both unimolecular and bimolecular reactions and is intimately involved in any system where highly vibrationally excited molecules play a role. Examples range from chemical lasers and combustion to surface etching with reactive species generated from highly vibrationally excited precursors.

Energy transfer in highly vibrationally excited polyatomic molecules is a fundamental process for which theoretical descriptions are far from complete.[1] Propensity rules that qualitatively describe the relaxation pathways in ground[2] and electronically excited[3] states of some systems are not universally applicable, as increasingly detailed experiments have begun to

reveal.[4] Theoretical models of collisional energy transfer in highly vibrationally excited molecules are even less well-developed than those for molecules containing little vibrational energy. The experiments described in this report are designed to provide data that can critically test and extend theoretical descriptions. Our goal is to characterize highly vibrationally excited molecules at the level of individual quantum states and to determine the rates and pathways of their collisional relaxation.

EXPERIMENTAL APPROACH AND RECENT RESULTS

We have demonstrated vibrational overtone excitation as a means of preparing highly vibrationally excited polyatomic molecules in single quantum states and have shown that laser induced fluorescence (LIF) is a means of probing the excited molecule during collisional relaxation.[5] Because one of the central features of energy transfer in highly energized species is the nature of the vibrationally excited state itself and how its identity affects the collisional relaxation rates and pathways, our work includes <u>characterization of the initially excited state</u>. The central goal of our effort is <u>the measurement of the rates and pathways</u> from these excited states by monitoring both the initially prepared state and the states into which collisions move population. Because our laser induced fluorescence detection technique involves an electronically excited state, we find it both necessary and advantageous to obtain information on <u>the electronically excited molecule</u> as well. This section describes all three aspects of our recent AFOSR sponsored research.

Our approach is to prepare a single rovibrational state by exciting a vibrational overtone transition with a pulsed laser and to interrogate the highly vibrationally excited molecule, either immediately after excitation or after a short time delay, with a second, ultraviolet laser. The excitation transition reaches a high vibrational level in the ground electronic state, and the probe transition is to the electronically excited state from which we observe fluorescence. Figure 1 is a generalized energy level

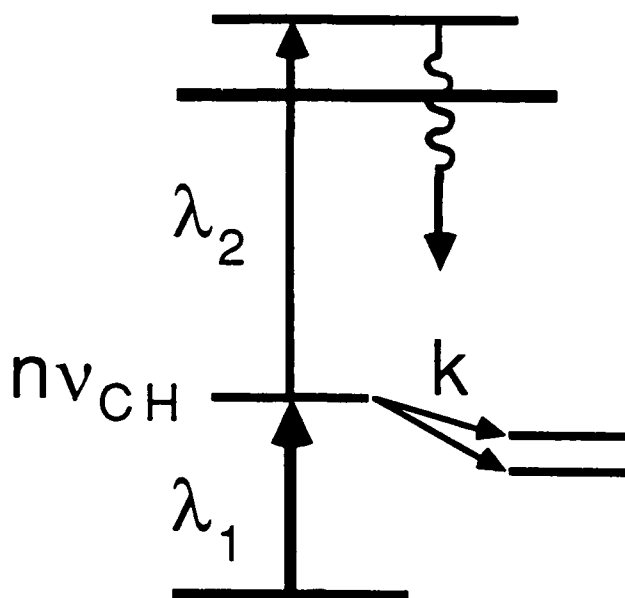diagram that illustrates the excitation and detection scheme.

Figure 1

Varying the wavelength λ_2 of the probe laser generates the laser
induced fluorescence excitation spectrum of the highly
vibrationally excited molecule, and, by selecting wavelengths
corresponding either to initially prepared or collisionally
populated states, we can monitor their time evolution. For
example, Figure 1 shows the situation in which collisional energy
transfer removes molecules from the initially populated state with
bimolecular rate constant k. This collisional depopulation
appears as a decrease in the LIF signal for longer intervals
between the pulse from the vibrational overtone excitation laser
(λ_1) and that from the probe laser (λ_2).

High Vibrational States

The local mode model of stretching vibrations involving light atoms describes the coarse features observed in vibrational overtone spectroscopy quite well,[6,7] but a complete description of the molecular eigenstates that can be prepared in small molecules requires an extension of the model to include other vibrational motions. A very useful picture,[8-10] which is similar to theories of radiationless transitions,[11] treats an anharmonic, high-frequency vibration, such as a CH, NH, or OH stretch, as the "bright" zero-order state that carries the vibrational overtone transition strength and couples that to the other "dark" zero-order states in the molecule. Figure 2 illustrates this model for small molecules. The coupling between the background states $\{|\ell\rangle\}$ and the bright zero-order state $|s\rangle$ produces the molecular eigenstates $\{|n\rangle\}$, each of which is an admixture of the inter-acting zero-order states,

$$|n\rangle = c_s^n|s\rangle + \sum_\ell c_\ell^n|\ell\rangle. \qquad (1)$$

The strength of the transitions in a spectrum depends on the amount of the character of the bright state, as determined by c_s^n, that each eigenstate possesses. The value of this model is its description of the eigenstates in terms of zero-order
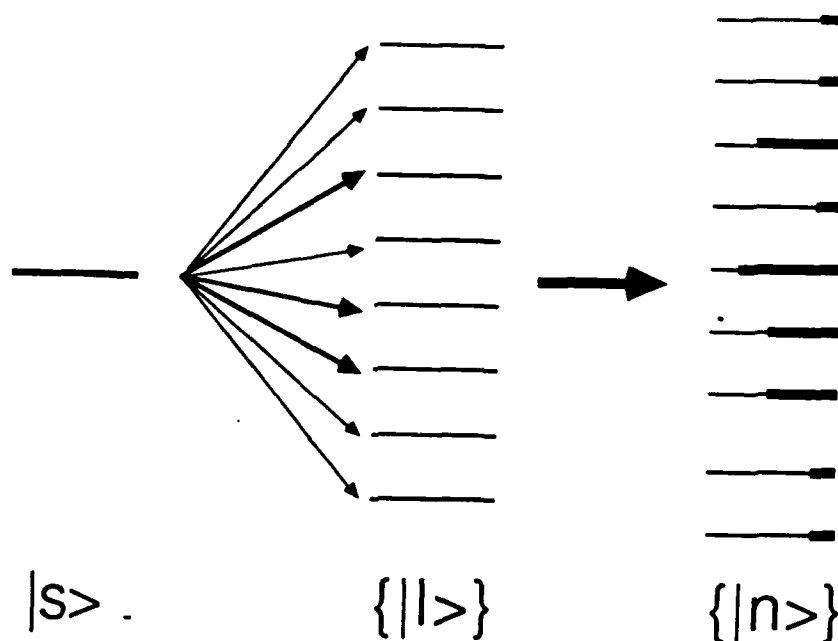
Figure 2

$|S>$. $\{|l>\}$ $\{|n>\}$

states about which one has good chemical intuition. This is

particularly useful in thinking about the vibrational overtone

excitation probability as arising from the local mode vibration of

a bond to a light atom and, as discussed below, in modelling

electronic excitations from vibrationally excited states using

Franck-Condon factors based on the zero-order states. Of course,

knowing the complete set of coefficients in eq. (1) allows one to

predict the time-evolution of the local mode zero-order state, if

it were to be prepared.[12,13] Because the goal of our work is to

monitor collisional energy transfer rates and pathways out of

individual molecular eigenstates, the description given above is

essential in understanding the states we initially prepare. In

addition, the probe step in our experiments selects out certain

zero-order states $|\lambda>$ that have large Franck-Condon factors in the

electronic excitation.

Probing Highly Vibrationally Excited Molecules

The intensity of a transition in the laser induced fluorescence excitation spectrum depends on the Franck-Condon overlap integral between the highly vibrationally excited, ground electronic state and the particular rovibrational level of the excited electronic state to which the the probe laser is tuned. One of the keys to our measurements, in which the vibrational overtone transition excites fewer than 10^{-5} of the molecules, is efficient discrimination against vibrationally unexcited species. As Figure 1 illustrates, we use probe laser photons that have only enough energy to reach the few lowest levels of the electronically excited state in transitions from highly vibrationally excited molecules. Because these photons are unable to excite molecules from low vibrational levels of the ground state, our detection scheme favors "off-diagonal" probe transitions in which a large geometry change produces good Franck-Condon factors between the vibrationally excited molecule in the ground electronic state and the vibrationally unexcited molecule in the excited electronic state. The Franck-Condon factors for off-diagonal transitions of vibrations involving light atoms are often small, since the bond lengths change little upon electronic excitation, but those for lower frequency vibrations can be larger. While the amount of the bright zero-order state $|s\rangle$ in an eigenstate determines its vibrational overtone excitation probability, the amount of a dark zero-order state $|\ell\rangle$ can determine the intensity of its

transitions in the probe step. This situation provides an experimental window on the nature of the initially prepared state. The intensity in the probe spectrum reflects the extent to which the eigenstate resembles the zero-order states that have favorable Franck-Condon factors in the electronic transition.

Our measurements on acetylene illustrate the means by which we probe highly vibrationally excited states. Figure 3 is an energy level diagram for the experiment, and Figure 4 is the photoacoustic absorption spectrum for acetylene showing transitions to single rotational states in the region of the second overtone of the CH stretching vibration ($3\nu_{CH}$). (The spectrum also contains small contributions from other vibrational transitions. We can simulate the complete spectrum using known band centers and rotational constants for C_2H_2.[14]) We set the wavelength (λ_1) of the vibrational overtone excitation light, which comes from stimulated Raman scattering of pulses from a Nd:YAG/dye laser in H_2, to a particular rotational line, such as the R(19) transition marked on the spectrum. Scanning the wavelength (λ_2) of a frequency-doubled, excimer/dye probe laser produces the LIF excitation spectrum for $C_2H_2(3\nu_{CH})$ shown in Figure 5. We obtain these data a low total pressures ($\approx$ 50 mTorr) and short delays ($\approx$ 10 ns) between the laser pulses to ensure that we observe only the initially prepared state.
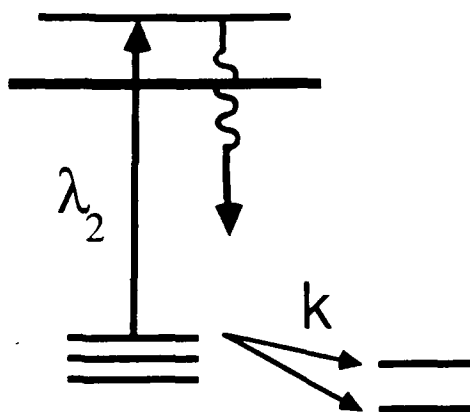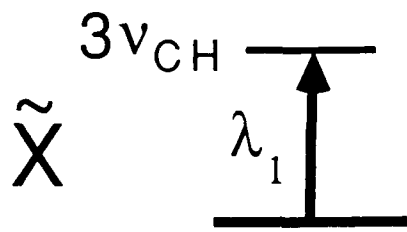
$\tilde{A}$

λ_2

Figure 3

$3\nu_{CH}$

$\tilde{X}$

λ_1

k

Figure 4

C_2H_2 ($3\nu_{CH}$) Photoacoustic Spectrum

R(J=7)

R(J=19)

1.044

Wavelength (μ)

1.030

LIF Excitation Scan

Excite $3\nu_{CH}$, R(J=19)
P = 0.050 Torr
Laser Delay = 10 ± 2 nsec

LIF Intensity

Figure 5

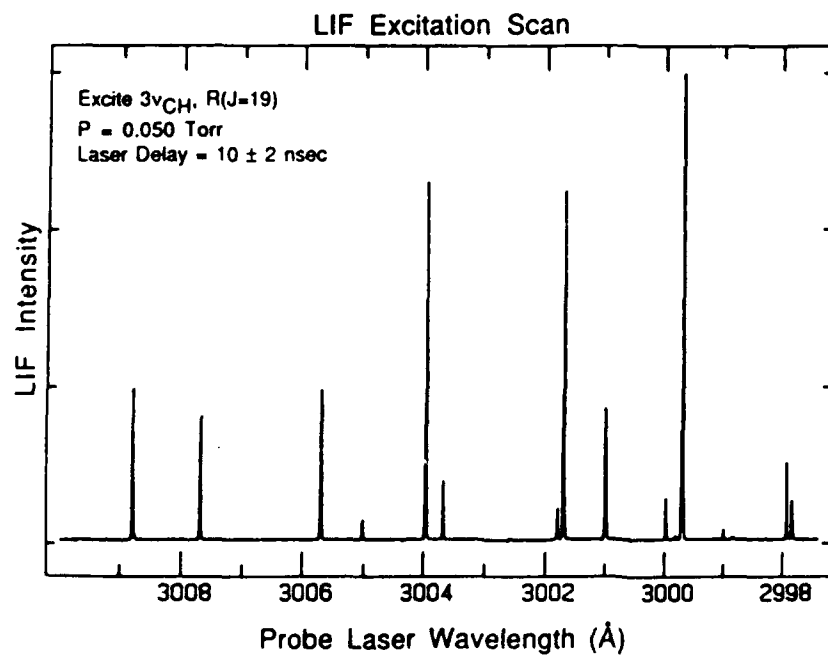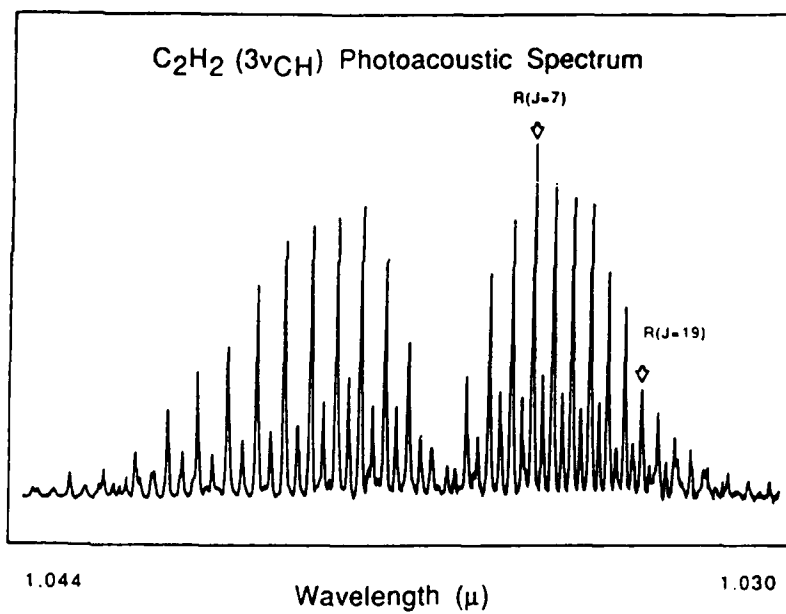3008   3006   3004   3002   3000   2998

Probe Laser Wavelength (Å)

The sharp features in the LIF excitation spectrum are transitions between single rotational states in the highly vibrationally excited and the electronically excited molecule. Because the ground electronic state of acetylene $(X\ ^1\Sigma_g^+)$ is linear and the excited electronic state that we access is <u>trans</u> bent $(\tilde{A}\ ^1A_u)$,[15] the <u>trans</u> bending vibration has particularly good off-diagonal Franck-Condon factors that lead to progressions in this vibration in resolved emission spectra.[16] In addition, the increased length of the C-C bond in the $\tilde{A}$ state produces a similar progression in that stretching vibration.[16] Thus, we expect that these are the two zero-order states $|\lambda\rangle$ that lead to the largest signal in the probe step, and we infer that the states we observe must possess significant <u>trans</u>-bending or CC stretching character.

The data in Figure 6 illustrate the trade between excitation and detection efficiency in our experiments. The upper trace (a) shows a portion of the photoacoustic vibrational overtone absorption spectrum in the region of the R(7) transition. The middle trace (b) shows that the laser induced fluorescence signal with a probe laser wavelength of λ_2 = 2988.17 A reproduces the photoacoustic signal. Changing the probe laser wavelength a small amount to λ_2 = 2988.19 A [trace (c)] alters the situation substantially. For this probe wavelength, the maximum in the excitation spectrum occurs in a region where the photoacoustic spectrum shows little absorption. Apparently, we are probing a state that has a smaller vibrational overtone excitation probability (less $|s\rangle$ character in terms of the zero-order state model) but a better

transition probability in the probe step. This is not an isolated occurrence, and we plan to explore such behavior as means of identifying states that have weak vibrational overtone transitions.
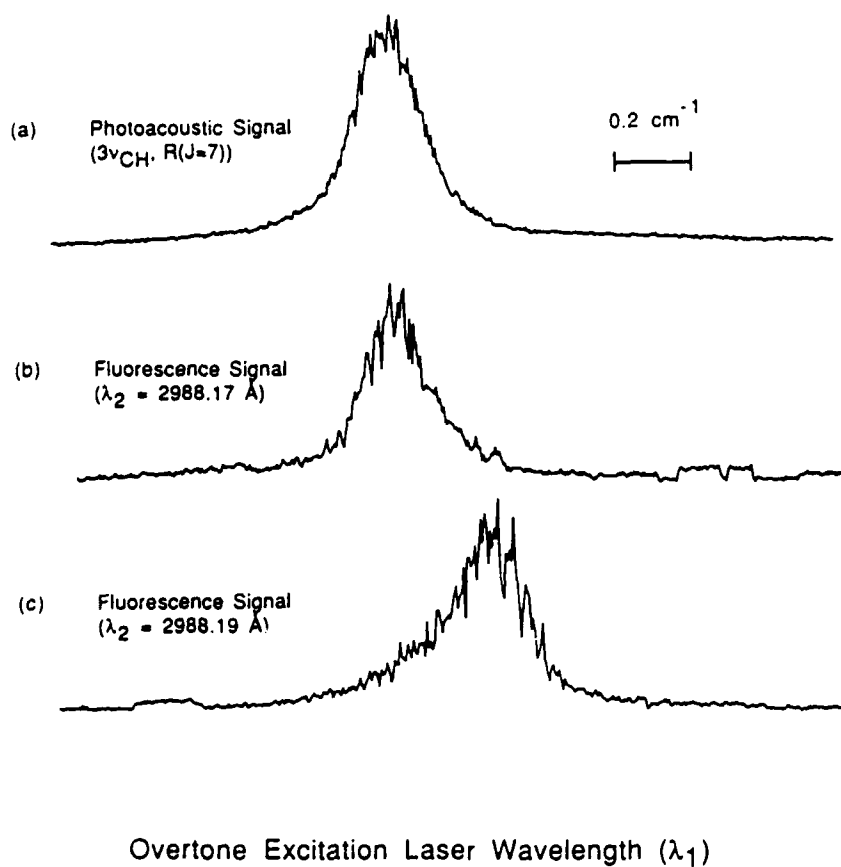
(a) Photoacoustic Signal
$(3\nu_{CH}, R(J=7))$

0.2 cm^{-1}

(b) Fluorescence Signal
$(\lambda_2 = 2988.17$ Å$)$

Figure 6

(c) Fluorescence Signal
$(\lambda_2 = 2988.19$ Å$)$

Overtone Excitation Laser Wavelength (λ_1)

Collisional Energy Transfer

We observe collisional energy transfer from single quantum states of highly vibrationally excited molecules by fixing the vibrational overtone excitation wavelength on a particular rotational transition and selecting a probe laser wavelength that induces fluorescence from the initially populated state. Varying the time delay between the two lasers reveals the time-evolution of the initially prepared state. We can tune the probe laser to monitor a collisionally populated state and observe the growth in population of that final state as well. Thus, we have the means of determining state resolved rates and collisional relaxation pathways in molecules containing over 100 kJ mol^{-1} of vibrational energy, as our measurements on acetylene demonstrate.

Figure 7 shows the LIF signal from an initially populated state of $C_2H_2(3\nu_{CH})$ for increasing delay times between the excitation and probe lasers. Fitting the decrease as a single exponential provides a psuedo-first order decay constant from which we extract the bimolecular relaxation rate constant for a single rotational state, as shown in Figure 8 for self-relaxation of $C_2H_2(3\nu_{CH}, J=20)$. These measurements on J=8 and J=20, which are summarized in Table I, show that the self-relaxation of C_2H_2 containing 9640 cm^{-1} of vibrational energy proceeds at about 70% of the gas kinetic collision rate and that the rates for the two rotational states are similar.[5] We have also measured the

Table I. Relaxation Rate Constants and Probabilities for C_2H_2 $(3\nu_{CH})^a$

	C_2H_2	He	Ar	Xe
J=8	12.0±1.4 (0.74)		5.2±1.1 (0.46)	
J=20	10.4±0.8 (0.64)	4.8±0.8 (0.35)	4.7±0.9 (0.42)	4.8±0.5 (0.38)

(a) Units of $\mu s^{-1} Torr^{-1}$. The uncertainties are two standard
deviations of the least squares fit to the slope of the
Stern-Volmer plots. The probabilities, given in parentheses,
are the ratio of the measured rate constant to the Lennard-
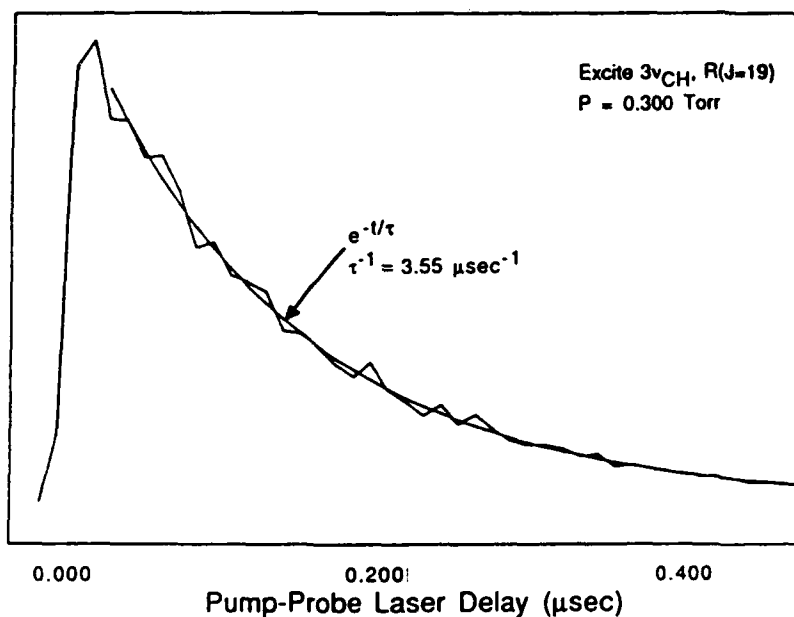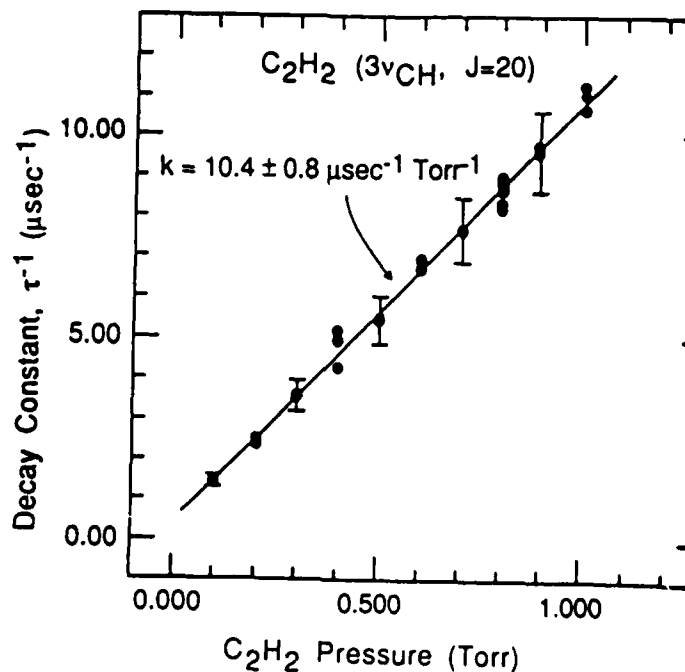Jones collision rate constant.

Figure 7

Figure 8

quenching by several rare gas partners in order to gain more insight into the relaxation mechanism. The rare gas partners He, Ar, and Xe all quench the J=20 state of $C_2H_2(3\nu_{CH})$ at essentially the same rate, which is about half of that for self-relaxation. The similarity of the probabilities for self-relaxation and for quenching by a rare gas indicates that intermolecular vibration-to-vibration energy transfer is not the relaxation pathway, since changing from a molecular to atomic collision partner should alter the rate drastically. This observation does not rule out the possibility of intramolecular vibration-to-vibration energy transfer or rotational energy transfer.

Our ability to monitor the arrival of population in final states should allow us to distinguish these two mechanisms, and we have made preliminary measurements in which we observe transitions from as yet unidentified collisionally populated states growing in at a rate that is comparable to the loss rate. Because the density of vibrational states in acetylene at 9600 cm^{-1} of excitation is about 3.1 per cm^{-1}, many states are close enough in energy to be populated by a collision that involves a very small change in vibrational energy content. In addition, intramolecular couplings of the type discussed above may enhance vibrational energy transfer.[14,17,17] These measurements on acetylene mark our implementation of a state resolved probe of collisional relaxation in highly vibrationally excited molecules and suggest the potential scope of the technique.

Vibrations in the Electronically Excited State

The involvement of an electronically excited state in our detection scheme creates both a complication and an opportunity. In some cases, we must sort out new electronic spectroscopy to completely analyze our measurements, but we have an opportunity to observe vibrations in the electronically excited state that are often inaccessible. Two features of our experiment make this possible. One is that the excitation in the probe step (see Figure 1) comes from states in a molecule that contains far more vibrational energy than available in a room-temperature sample. Thus, transitions that appear only as very weak hot-bands in a conventional experiment might be quite strong in our measurement. The other differentiating feature is that we reach the electronic state by a two-photon process, one for vibrational overtone excitation and one for the subsequent electronic excitation. In molecules of high symmetry, this makes available a set of vibrations of the excited state that are unobservable in the one-photon electronic excitation. Because the first transition is solely on the ground electronic surface, we can easily perform two-photon measurements on the lowest electronically excited state. The excitation goes through a real state of known vibrational symmetry and, hence, reaches a limited subset of the available vibrations in the excited state.

Figure 9 illustrates this aspect of our technique for acetylene. The first excitation from the vibrationally unexcited molecule prepares a vibration of B_u symmetry in the A_g ground

electronic state. (The Σ_g^+ ground electronic state is A_g in the reduced symmetry of the C_{2h} point group of the bent electronically excited state.) In the absence of collisions, the second transition reaches a B_u vibration in the A_u electronically excited state, compared to one-photon transitions that can excite only A_g vibrations. Even hot-band excitations, which can produce

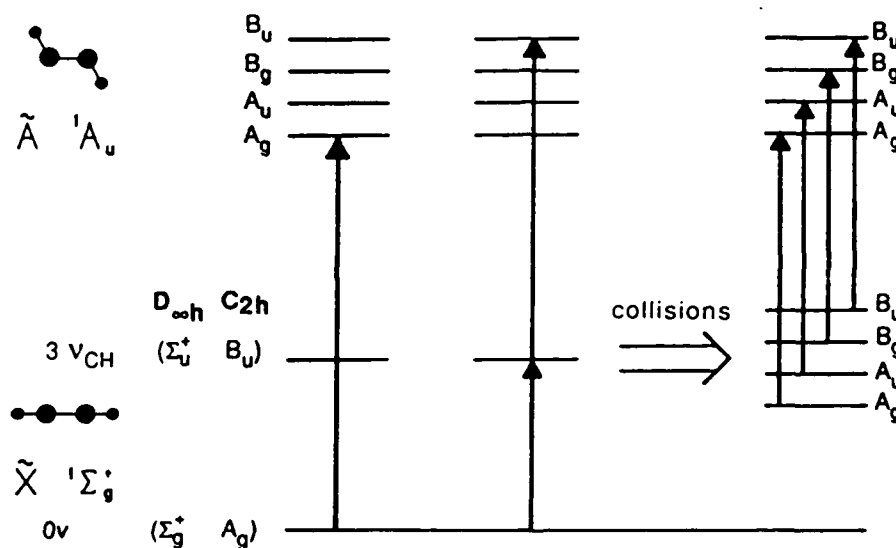## SYMMETRY ALLOWED TRANSITIONS

Figure 9

vibrations of B symmetry, are restricted to gerade states by the one-photon dipole selection rules. (This simple analysis leaves out the complication of vibronic coupling to other electronic states, which seems unimportant in acetylene.)

We have used this approach to excite the B_u cis-bending vibration (ν_6) in the electronically excited state of acetylene directly. This state and the A_u torsional vibration (ν_4) have

only been observed as two-quantum perturbations in resolved laser induced emission experiments,[16] where the two-observed transitions cannot be assigned directly but must be differentiated on the basis of theoretical calculations. In our experiments, excitation of the B_u bending vibration is possible in the absence of collisions, and the A_u torsion appears only after collisions populate an A_u vibration in the ground electronic state. Our preliminary analysis of the excitation spectra in the absence of collisions suggests a reversal of the assignments of the ν_4 and ν_6 vibrations inferred from the perturbation analysis.[16] This direct observation of these states is an important ancillary benefit of using laser induced fluorescence to probe highly vibrationally excited molecules. Our detection scheme, which requires extensive information about the electronically excited state from independent spectroscopic studies, can occasionally add to that body of knowledge.

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Publications Since 1985 Supported by AFOSR

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5.   Collisional Relaxation of Single Rotational States in Highly
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     Utz, and F.F. Crim, J. Chem. Phys. 88, 5976 (1988).